

TEMPERATURE EFFECTS ON COAL LIQUEFACTION; RATES OF DEPOLYMERIZATION
AND PRODUCT QUALITY AS DETERMINED BY GEL PERMEATION CHROMATOGRAPHY

by

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INTRODUCTION

In this paper the reactor temperature and residence time effects on the depolymerization of coal will be discussed. The ratio of the absorbances of the 950 molecular weight (MW) to 280 MW peaks observed in the gel permeation high pressure liquid chromatography (HPLC) separation of products has indicated use as a measure of depolymerization and product quality.

Research on the non-catalytic CO-Steam liquefaction of coal was initiated at the Grand Forks Energy Research Center (GFERC) in 1974 as a continuation of research started at the Pittsburgh Energy Research Center (PERC). The objective is to develop the process as a commercial, economic method to produce a stable coal liquid which will meet environmental requirements (ash, nitrogen, and sulfur contents) for use as a boiler fuel. The research program has followed three overlapping stages: 1) Batch autoclave research, 2) 3-lb/hr continuous process unit operation, and 3) process development unit scaleup based on findings from (1) and (2). Selected data from item (1) will be considered in this paper.

The batch autoclave consists of a batch reactor system that can be charged with room temperature slurry to a hot (up to 500° C) reactor which can be sampled (both liquid and gas phases) at various times to determine reactant and product changes. Figure 1 depicts the fractions that are obtained during analysis. This system is also being utilized to determine total gas content of slurry at up to 4500 psig and 480° C. The amount of the material charged that is found in the gas phase in the reactor at various temperatures and pressures has been determined, and the effects of slow (1 hour) or rapid (3 minute) heatup of slurries to reaction temperature on molecular weight distributions and coking is being studied.

Undistilled coal products (solvent refined coals and coal liquids) analyzed at GFERC have contained 10 to 80 pct volatiles at 1 torr and 250° C. This volatile material is readily analyzed by GC, GC-MS, or low voltage MS. Approximately 50 to 80 pct of the non-volatile fraction was readily soluble in tetrahydrofuran (THF). Analysis of a 1 w/w pct solution of this non-volatile fraction (after passing through a 0.5 μ filter) has yielded molecular weight distributions which are not masked by solvent or light organic material. The technique has enabled the determination of the rate of disappearance of high molecular weight materials as a function of reactor temperature and residence time.

EXPERIMENTAL

Gas-Slurry Charge Composition

The one-liter reactor was typically charged with 250 gms of slurry (from a cylinder to the reactor using gas pressure). The amount of gas charged was approximately 3.5 moles. Molecular weight distributions have been found to be essentially independent of whether the charge gas was CO or synthesis gas (50:50 hydrogen to carbon monoxide). For the data reported, 250 gms of slurry were charged. The slurry composition was as follows:

27.3% as-received coal
8.0% of water added
58.2% anthracene oil
6.5% tetralin

Proximate and ultimate analysis for the lignite used in these studies is presented in Table 1.

TABLE 1. - Beulah Standard 2; GF 77-712

	Coal (As received)	Coal (Moisture free)	Coal (Moisture and ash free)
Proximate analysis, pct:			
Moisture.....	27.80	--	--
Volatile matter.....	30.45	42.18	46.93
Fixed carbon.....	34.45	47.71	53.07
Ash.....	7.30	10.11	--
TOTAL	100.00	100.00	100.00
Ultimate analysis, pct:			
Hydrogen.....	6.09	4.16	4.63
Carbon.....	46.30	64.14	71.35
Nitrogen.....	0.72	1.00	1.11
Oxygen.....	39.03	19.82	22.05
Sulphur.....	0.56	0.77	0.86
Ash.....	7.30	10.11	--
TOTAL	100.00	100.00	100.00

Molecular Weight Distribution Determinations

The equipment used to determine molecular weight distributions was a Waters Model ALC-GPC-201 system fitted with one 500 and three 100 Å microstiyragel columns. CO-Steam product samples were first distilled at 250° C and 1 torr to remove volatile material. A 1 w/w pct tetrahydrofuran (THF) solution of

the non-distillable material was passed through a 0.5 μ filter prior to injection. The percent THF insoluble residue was compared to THF solubility data obtained for a sample that was not subjected to distillation. A quotient of stability to distillation can be calculated which reflects the fraction of the original THF soluble material that was still soluble after distillation at 250° C and 1 torr. This stability quotient has been found to increase with reactor residence time and temperature.

In run 30, the reactor was charged cold and heated to 400 \pm 2° C in 92 minutes and held at this temperature for 1/2 hour. The reactor was subsequently heated to and held in steps at 435 \pm 4° C and 475 \pm 5° C.

In Table 2, data from run 30 are presented. The stability quotient increased from 22 to 56 pct in 19 minutes at 400° C. In going to 437° C the quotient goes to 71 pct and for the next 104 minutes remained essentially constant. The stability quotient also reflects the quantity of sample that is analyzed by HPLC after distillation.

TABLE 2. - Product stability to distillation versus residence time and temperature in run 30

Sample No.	Temp., °C	Time	Product fractions		Stability quotient, pct ^{b/}
			(1) THF Insoluble, pct ^{a/}	(2) Non-distillable, pct ^{a/}	
1 3	400° \pm 2°	92			
		94	11	22	22
		113	6	18	56
4 6	435° \pm 4°	141			
		142	7	22	71
		182	9	20	78
7 9	475° \pm 5°	200			
		212	8	23	74
		246	11	29	73

a/ The values for (1) and (2) are percents of total reactor slurry product obtained at reactor temperature and pressure.

b/ The stability quotient is the percent of (2) minus (1) that was soluble after distillation at 250° C and 1 mm Hg.

The molecular weight distributions were measured relative to commercially available standards (purchased from Waters) to enable comparison by other researchers. Detection was by UV at 254 nm.

RESULTS AND DISCUSSION

The temperature at which the reactor was operated has had dramatic effects on the molecular weight distribution obtained for the non-distillable, THF soluble fraction of coal liquefaction products.

Figure 2 depicts the molecular weight distributions obtained at 400, 435 to 450, and 460 to 480° C for residence times under 1/2 hour. These distributions have been observed in experiments where the reactor was heated to temperature in 3 minutes or in 1 hour. Figure 2 illustrates the rapid decrease in the absorbance at molecular weights greater than 750 and the shift of the average molecular weight of this fraction from over 600 at 400° C to about 500 at 440-450° C and finally to about 300 at 460 to 480° C. Since the absorbance is proportional to concentration, ratios of the absorbance maximum between 1200 and 950 to the value at 280 MW (A_{950}/A_{280}) have been used to correlate data from various experiments. This ratio has also been found to be independent of experimental errors in preparing 1 w/w pct solutions. In Figure 3, the ratios obtained for samples removed for under 1/2 hour residence times during 1/2 hour residence time for a number of experiments are depicted versus reactor temperature.

High ratios indicate large concentrations of over 750 MW molecular weight material. The rapid decrease of the ratio with temperature indicates that reactors operated at higher temperatures produce products with lower average molecular weights.

Rates of Depolymerization

The change in molecular weight distribution with reactor residence time can be used as a qualitative measure of the rates of depolymerization at different temperatures. At 400° C the molecular weight distribution changes little with time (Fig. 2). However, the stability to distillation does increase, (Table 2) which indicates that the quality of the product increases with residence time. Change in product at 400° C have not been studied to any degree since the molecular distribution observed is similar to that of solvent refined coals, which are not liquids at room temperature.

At temperatures of 435 to 450° C notable residence time effects have been observed especially in the greater than 750 MW material. Figure 4 presents two ratios (A_{950}/A_{250} and A_{450}/A_{280}) versus residence time for an extended experiment in which the reactants were initially heated to 440° C in three minutes and held there for 1/2 hour, followed by stepwise heating during 5-10 minutes and holding for 1/2 hour at 450, 460, and 470° C. After 30 minutes at 440° C, the ratio A_{950}/A_{250} tends to level off. The changes observed were on similar fractions of total product. The molecular weight distribution and the ratios observed at 440° C were similar to those observed for CO-Steam product prepared at PERC.

A rapid decrease in the A_{950}/A_{280} ratio occurred within 7 minutes of heating from 440° to 450° C. Additional time at 450° C yielded little change in the ratio. The A_{450}/A_{280} ratio also leveled off. Molecular weight distributions for this material indicated that no recoverable material greater than 1000 MW was present; however, the distribution did have a shoulder at 950 MW. These results are similar to those obtained for coal liquids produced by the Synthoil Process.

Subsequent heating to 460° C caused an additional decrease in both the A_{950}/A_{280} and A_{460}/A_{280} ratios, with little change continuing after 15 minutes. Little further change has been observed in these molecular weight distributions in other experiments at 470° C for 1 hour or at 480° C for 1/2 hour. Similar distributions have been obtained for samples made by the SRC II Process.

The most dramatic decrease in molecular weight occurred during heating from 440 to 450° C. However a further beneficial decrease occurs between 450 to 470° C. Depolymerization occurs very rapidly at 460° C, and the 300 MW material produced does not depolymerize further with time beyond 15 minutes.

Product Quality

Other research being conducted at GFERC has indicated that there is direct dependence of viscosity on the average molecular weight and the concentration of pre-asphaltene material.¹ Asphaltene content in higher concentrations has also effected increased viscosities of coal products.^{2,3,4} Figure 5 depicts the molecular weight distributions of pre-asphaltene and asphaltene fractions obtained from PERC CO-Steam, SRC II, and the GFERC product produced at 470° C. For each product, the asphaltene fraction has a lower average molecular weight than the pre-asphaltene fraction. Absorbance at 950 MW is most indicative of the presence of the higher MW pre-asphaltene and asphaltene material, and that at 280 MW of lighter non-distillable material.

The A_{950}/A_{280} ratio should correlate well with the viscosity for a totally coal derived product. The A_{460}/A_{280} ratio should be useful as a measure of product quality after the absorbance at 950 MW approaches zero.

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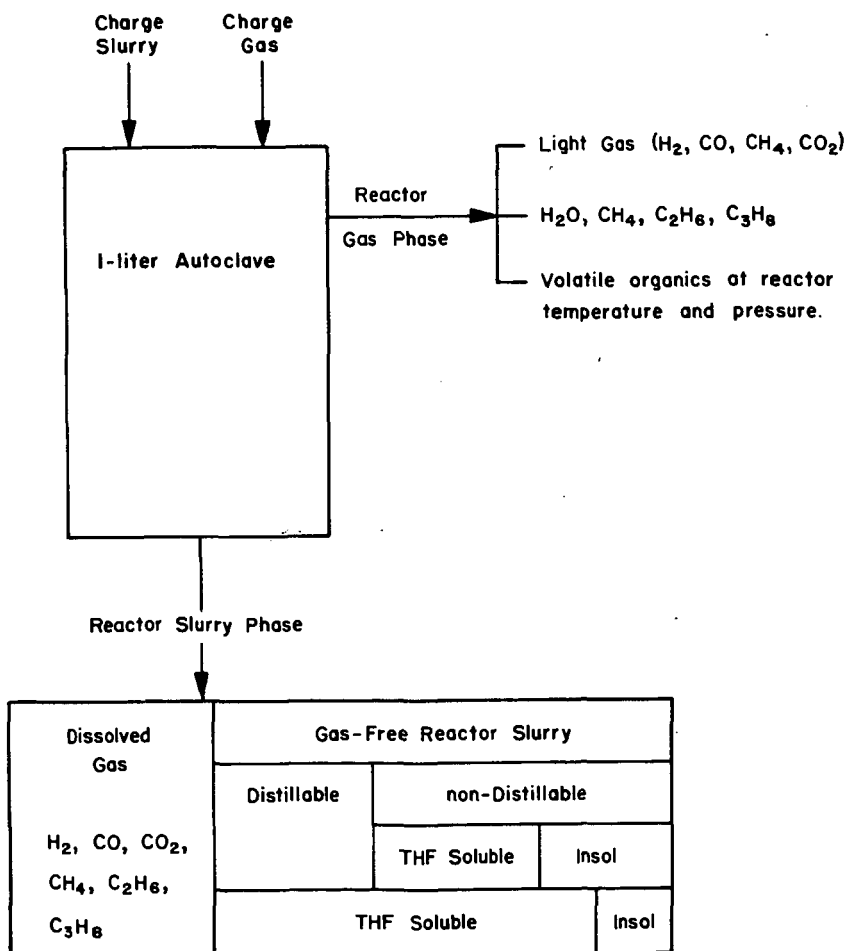


FIGURE 1. - Major sample fractions derived from batch autoclave studies on CO-Steam kinetics.

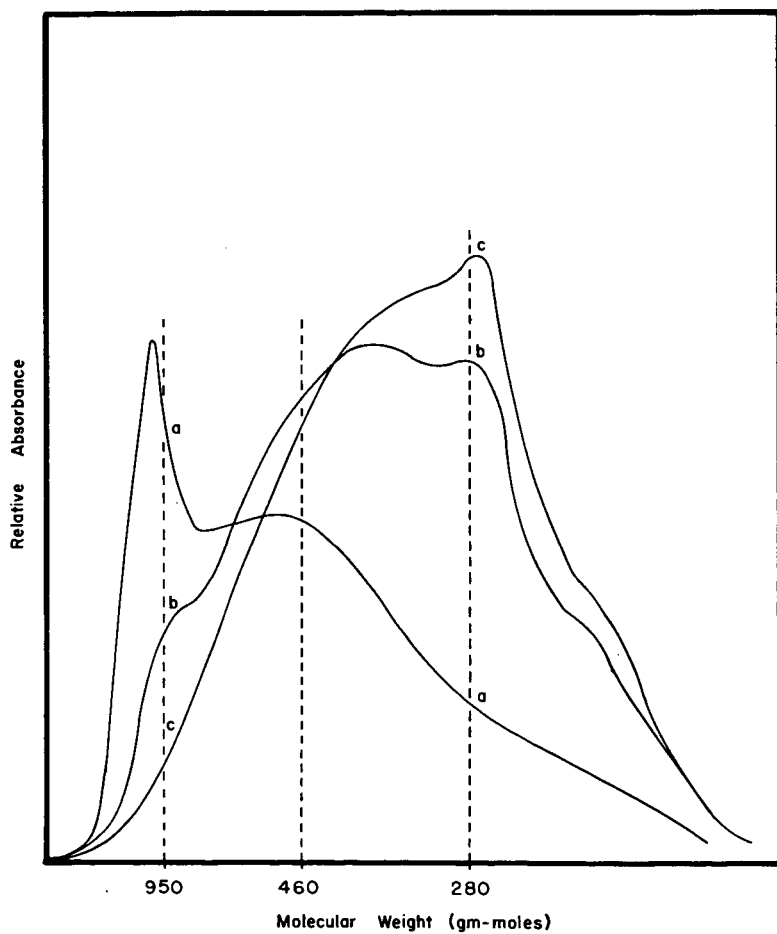


FIGURE 2. - Average MW distributions obtained at a) 400° C, b) 440-460° C, and c) 460-480° C for the non-distillable, THF soluble fractions of coal liquid products.

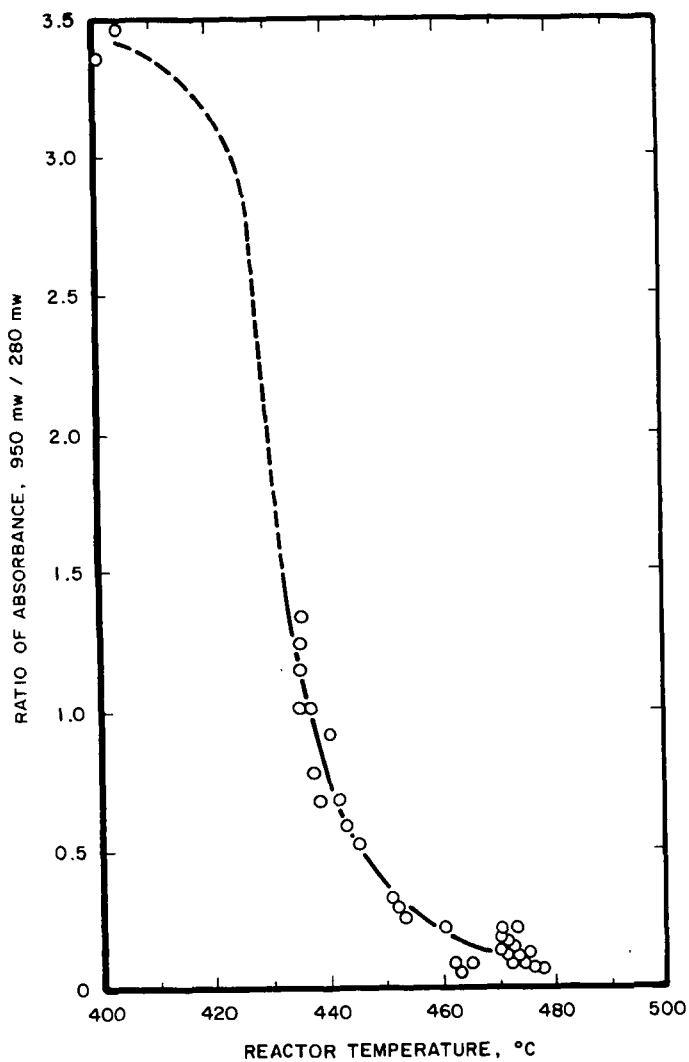


FIGURE 3. - Correlation of the A_{950}/A_{280} ratio to reactor temperatures for residence times under one-half hour.

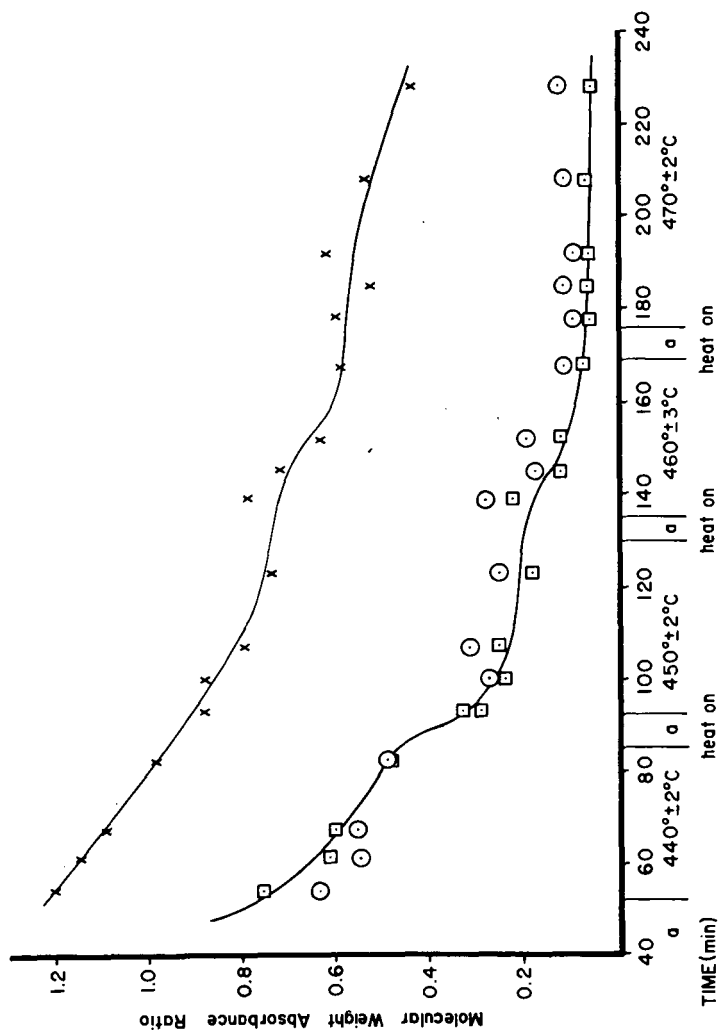


FIGURE 4. - Molecular weight absorbance ratios versus time at various temperatures. (A950/A280 = □; A460/A280 = ○) During time interval "a" the temperature is increasing.

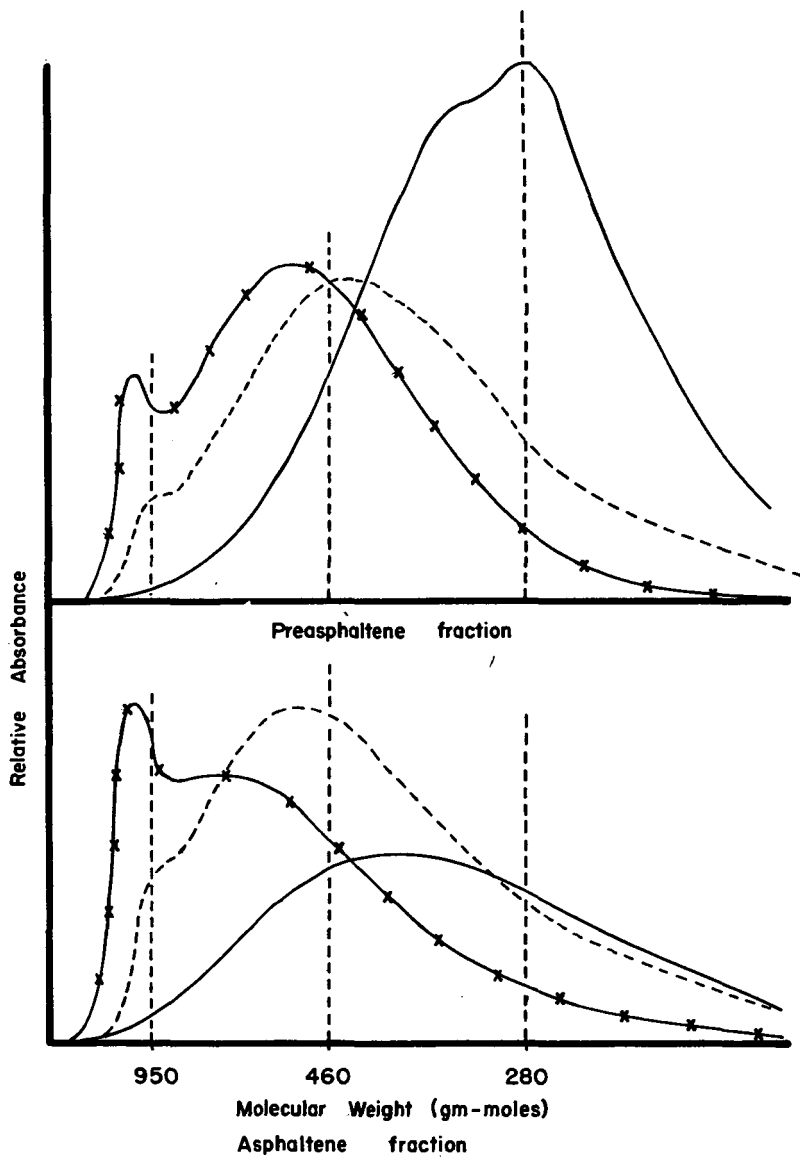


FIGURE 5. - Comparison of molecular weight distributions for coal liquid fractions obtained from PERC CO-Steam (x-x), SRC II (----) and GFERC, 470° C (—) samples.